

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 799 871 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
08.10.1997 Bulletin 1997/41

(51) Int Cl.⁶ **C09D 11/10, C08F 290/14**

(21) Application number: **97302126.4**

(22) Date of filing: **21.03.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**

(30) Priority: **02.04.1996 GB 9606966**

(71) Applicant: **SERICOL LIMITED
Broadstairs, Kent CT10 2PA (GB)**

(72) Inventors:
• **Gould, Nigel Paul
Broadstairs, Kent CT10 2TH (GB)**

• **Abbasi, Fereidoun
Margate, Kent CT9 3HT (GB)**

(74) Representative: **Lewis, Pauline Therese et al
Burmah Castrol Trading Limited,
Group Patents Department,
Burmah Castrol House,
Pipers Way
Swindon, Wiltshire SN3 1RE (GB)**

(54) **UV-curable printing ink**

(57) A water-based, UV-curable ink for plastic sub-
strates, comprising:

a) a water-dispersible or water-soluble urethane

acrylate oligomer;

b) a monomer that is capable of softening the sub-
strate in part or in full; the monomer being resistant
to hydrolysis; and

c) a passive resin that is soluble in the monomer.

EP 0 799 871 A1

Description

The present invention concerns a printing ink, and in particular a water-based, UV-curable printing ink that is capable of adhering to plastic substrates.

A typical water-based, UV-curable ink currently on the market comprises: a non-ionic water soluble urethane acrylate; monomers such as tripropylene glycol diacrylate ('TPGDA') and ethoxylated trimethylol propane triacrylate ('ETMPTA'); water; a thickener; photoinitiators; flow aids; and pigments. The ink can be printed on to paper and board substrates through a plain weave mesh having a 150/cm mesh count. The inks exhibit good adhesion to paper and board substrates. Adhesion to substrates can be tested by scratching the dried ink with a fingernail and observing whether any ink is removed. If the ink is printed on to plastic substrates such as PVC or polystyrene, the adhesion is very poor and the ink can be easily removed by scratching.

The present invention is concerned with the problem of providing a water-based, UV-curable printing ink that exhibits improved adhesion to plastic substrates such as PVC and polystyrene.

In accordance with the present invention there is provided a water-based, UV-curable ink that is capable of adhering to a plastic substrate, comprising:

- a) a water-dispersible or water-soluble urethane acrylate oligomer;
- b) a monomer that is capable of softening the substrate in part or in full; the monomer being resistant to hydrolysis; and
- c) a passive resin that is soluble in the monomer.

In accordance with the present invention there is provided a method for preparing a water-based, UV-curable ink that is capable of adhering to a plastic substrate, the method comprising the steps of:

- a) selecting a monomer that is capable of softening the plastic substrate in part or in full and is resistant to hydrolysis;
- b) selecting a passive resin that is soluble in the monomer;
- c) dissolving the passive resin in the monomer;
- d) blending the passive resin and the monomer with a water-dispersible or water-soluble urethane acrylate oligomer; and
- e) adding water to the blend.

The water-based, UV-curable ink preferably comprises:

- a) from 3 to 30 %, preferably from 10 to 20 %, by weight of the water-dispersible or water-soluble urethane acrylate oligomer;
- b) from 10 to 50 %, preferably from 25 to 35 %, by weight of the monomer that is capable of softening the substrate in part or in full and is resistant to hydrolysis; and
- c) from 1 to 25 %, preferably from 5 to 15 %, by weight of the passive resin that is soluble in the monomer.

By the term 'passive resin' we mean a resin that would not substantially take part in a free radical, photopolymerisation reaction.

The inventors of the present invention have found a water-based, UV-curable ink that exhibits adhesion to plastic substrates such as polystyrene and PVC.

The monomer is preferably hexane diol diacrylate ('HDDA'). HDDA is a difunctional acrylate that offers a high cure rate. HDDA also exhibits excellent compatibility with and solvency for other resins and additives used in the ink.

The passive resin is preferably selected from the following list: solid epoxies, ketone resins, acrylate and methacrylate copolymers, vinyl resins, solid polyesters, phenoxy resins and cellulosics. The most preferred passive resins are acrylate or methacrylate copolymers.

The resin preferably has a Tg between 30 and 130°C.

Preferably at least 25 parts by weight of resin are dissolved in the monomer.

The ink preferably comprises at least 10%, more preferably at least 18%, even more preferably at least 25%, of water, based on the total weight of the ink.

The passive resin is preferably present in the ink in an amount from 1-25%, more preferably from 5-15%, by total weight.

The ink is preferably prepared by dissolving the selected passive resin in the monomer, and then adding the other components of the ink to the dissolved resin. A normal mechanical stirrer is used to disperse the components. A special high shear mixer is not required.

The ink can include any of the usual additives that are present such as: pigments, surfactants, UV stabilisers,

photoinitiators and synergists, waxes, rheology modifiers, and other commonly used monomers and oligomers.

Examples

Tests to Find a Suitable Monomer

Test for Monomer's Ability to Soften a Plastic Substrate:

In order to test whether any of the selection of monomers listed below are capable of softening plastic substrates such as polystyrene and self-adhesive PVC, a small drop of each of the monomers was placed on to polystyrene and PVC substrates. After being left for 5 minutes, the monomers were removed from the substrates using a soft cloth and the surface of the substrates was examined for softening and marking. The results are as follows:

Monomer	Polystyrene	Self-Adhesive PVC (Mactac 8129)
Tripolypropylene glycol diacrylate	no mark	no mark
Ethoxylated trimethylol propane triacrylate	no mark	no mark
Trimethyl propane triacrylate	no mark	no mark
2 phenoxyethyl acrylate	no mark	substrate softened
Di-propylene glycol diacrylate	no mark	no mark
N vinyl caprolactam*	substrate softened	substrate softened
N N di-vinyl imidazole*	substrate softened	substrate softened
N vinyl pyrrolidone	substrate softened	substrate softened
Hexane diol diacrylate	substrate softened	substrate softened
N vinyl formamide	substrate softened	substrate softened
Neopentyl glycol diacrylate	no mark	no mark
Octyldecyl acrylate	no mark	substrate softened
* 30% solutions in TPGDA since they are solid at ambient temperature.		

The results show that only five out of the twelve monomers that were tested were capable of softening both plastic substrates.

Test For Monomer's Hydrolysis Resistance:

In order for the monomer to be used in a water-based ink, it needs to be resistant to hydrolysis. The five monomers that were capable of softening the polyolefin were tested for their resistance to hydrolysis. The monomers were tested for their hydrolytic stability under both acidic and basic conditions. Ten percent dispersions of the monomers were prepared in deionised water, with the pH being adjusted to 5 and 9 with dilute HCl and NaOH respectively. The samples were stored for 1 week at 40 °C and then checked for degradation using HPLC. Of the monomers tested, hexane diol diacrylate (HDDA) gave the best resistance properties.

Test for Monomer's Compatibility with other Components in the Ink:

The monomer's compatibility with other components in the ink was tested by formulating the ink and checking for general problems such as separation on storage. The test was carried out using HDDA and the HDDA was found to be compatible with the ink's other components.

Tests to find a Suitable Passive Resin

Test for Solubility in Monomer:

In the inks of the present invention, the passive resin must be soluble in the monomer. To test whether a selection of resins were soluble in HDDA, 25% solids solutions of a range of passive resin types were prepared in HDDA and the solutions were examined for clarity and stability towards separation. The solubility is largely linked to molecular weight within a group of similar resins: the lower molecular weight examples have the best solubility.

The test revealed that the following passive resins are suitable for incorporation into the inks of the present invention: solid epoxies, ketone resins, acrylate and methacrylate copolymers, vinyl resins, solid polyesters, phenoxy resins and cellulose. The most preferred passive resins are acrylate or methacrylate copolymers.

Adhesion Test:

A selection of passive resins were incorporated into inks, and the inks were tested for their adhesion to a polystyrene substrate. The inks were made by initially preparing a 25% solids solution of the resin in HDDA. The other components of the ink were added sequentially while stirring with a mechanical stirrer. A formula similar to Example 1 below was used.

The inks were screen printed through a 150 plain weave mesh on to a polystyrene substrate. The films were cured at 30 m/min using 2 lamps at full power (Svecia UV drier, 2 80w/cm medium mercury lamps). After the films were dried, they were examined for adhesion by scratching the films with a finger nail and observing whether the film was damaged or removed. The results are as follows:

Resin	Type	Result
Paraloid B66 (sold by CHEMAC)	Methacrylate copolymer	Excellent film that could not be removed by scratching
Plexigum M345 (sold by Huls)	Methacrylate copolymer	Excellent film that could not be removed by scratching
Adhesion resin LTH (sold by Huls)	Polyester	Good film that could only be removed with difficulty by scratching
Synthetic resin 8K (sold by Huls)	Ketone	Fair adhesion but film could be removed by scratching
Surcol 836 (sold by Allied Colloids Limited)	Methacrylate copolymer	Good film that could only be removed with difficulty by scratching
CAB 381 (sold by EGGAR)	Cellulosic	Poor film that could easily be removed
Epikote 1001 (sold by SHELL)	Epoxy	Poor film that could easily be removed
Paphen-phenoxy PKHH (sold by Phenoxy Associates)	Phenoxy	Good film that could only be removed with difficulty by scratching

As can be seen from the results in the above table, the best results were given by acrylate and methacrylate copolymers, phenoxy resins and solid polyester resins. The methacrylate copolymers exhibited the best combination of results for adhesion, solubility in the monomer and hydrolytic solubility. Further tests showed that hard, high T_g polymers exhibited the best adhesion results:

Hydrolytic Stability:

Resins were not tested for their hydrolytic stability in isolation. No particular problems were encountered with hydrolytic stability of the resins used in the previous tests. Methacrylate copolymers were selected on the basis that their other properties were suitable and that they are well known for their hydrolytic stability. Experimental ink samples were however checked for changes in pH on storage. A decrease in pH indicates hydrolysis problems.

Determination of Water Content

The following test was used to determine the required water content for the ink: A range of experimental inks were prepared with a water content ranging from 10% to 45%. The viscosities were adjusted using HDDA so that all of the inks were identical. The inks were printed through 150 plain weave mesh on to 500 micron polystyrene substrate. The films were cured with 1 pass through a Svecia UV drier at 25 m/min (2x 80w/cm medium pressure mercury lamps). The films were compared for their hardness and adhesion by scratching the films with a fingernail. The maximum water level giving acceptable adhesion was determined. A level of approximately 25% was found to give excellent adhesion and an excellent film weight. Higher levels of water can be used but problems with water retention in the film occur and a predry stage may be required before UV curing.

Preparation and Testing of Inks

The following inks were prepared:

Example 1

Plexigum M345 ¹	6.0
Hexane diol diacrylate	28.3
Surfactant	1.0
Water soluble urethane acrylate oligomer	12.6

Water	25.0
Isopropyl thioxanthone	0.49
Irgacure 184	2.93
Amine synergist	1.98
Di trimethylol propane tetra acrylate	8.0
Magenta pigment base ²	13.0
UV stabiliser	0.7
Total	100.0

¹ Available from Huls

Example 2

5	Paraloid B66 ³	6.0
	Hexane diol diacrylate	28.3
	Surfactant	1.0
10	Water soluble urethane acrylate oligomer	12.6
	Water	25.0
	Isopropyl thioxanthone	0.49
15	Irgacure 184	2.93
	Amine synergist	1.98
	Di trimethylol propane tetra acrylate	8.0
20	Magenta pigment base ²	13.0
	UV stabiliser	0.7
	Total	100.0

³ Available from CHEMAC

30	² <u>Magenta pigment base:</u>	
	Polyester urethane acrylate	37.64
	Tripropylene glycol diacrylate	37.09
35	UV stabiliser	0.18

40	Sunfast magenta 228 0013	19.64
45	Cromophthal red BRN	5.45

Comparative Example 1

50	Water soluble urethane acrylate oligomer	35.0
	Tripropylene glycol diacrylate	14.0
	Irgacure 184	2.0
	Silicone flow aid	1.0
55	Surfactant	1.0
	Magenta pigment	2.5
	Water	43.5

(continued)

UV stabiliser	1.0
Total	100.0

Comparative Example 2

Water soluble urethane acrylate oligomer	35.0
Hexane diol diacrylate	14.0
Irgacure 184	2.0
Silicone flow aid	1.0
Surfactant	1.0
Magenta pigment	2.5
Water	43.5
UV stabiliser	1.0
Total	100.0

Comparative Example 3

Plexigum M345	6.0
N-vinyl caprolactam	18.3
Ethoxylated trimethylol propane triacrylate	10.0
Surfactant	1.0
Water soluble urethane acrylate	12.6
Water	25.0
Isopropyl thioxanthone	0.49
Irgacure 184	2.93
Amine synergist	1.98
Di trimethylol propane tetra acrylate	8.0
Magenta pigment base ²	13.0
UV stabiliser	0.7
Total	100.0

The inks were printed as before using a 150 plain weave mesh and a selection of substrates. The films were dried using a Svecia UV drier (2 x 80w/cm mercury lamps).

The inks were tested for their adhesion to plastic substrates using the following methods:

- fingemail scratch test as previously described; and
- cross hatch tape adhesion: The films were scored using a scalpel so that a block of one hundred 1 mm squares were produced. A small piece of adhesive tape was fixed securely over the scored area and removed with a swift

wrist action. The adhesion is gauged by the number of small squares removed from the substrate.

Results

Ink	Adhesion to Plastic Substrates
Example 1	Excellent adhesion to plastic substrates including self-adhesive PVC, rigid PVC and polystyrene
Example 2	Excellent adhesion to plastic substrates including self-adhesive PVC, rigid PVC and polystyrene

Comparative Example 1	Extremely poor adhesion to plastic substrates
Comparative Example 2	Exhibited only limited adhesion to some plastic substrates such as self-adhesive PVC
Comparative Example 3	Exhibited excellent adhesion to plastic substrates such as self-adhesive PVC, rigid PVC and polystyrene; however, ageing of the wet ink at 40 °C for 4 weeks caused the ink to exhibit poor adhesion because of poor hydrolysis resistance.

The above results clearly show that only inks falling within the present invention exhibit good adhesion to plastic substrates such as self-adhesive PVC, rigid PVC and polystyrene.

Claims

1. A water-based, UV-curable ink for plastic substrates, comprising:
 - a) a water-dispersible or water-soluble urethane acrylate oligomer;
 - b) a monomer that is capable of softening the substrate in part or in full; the monomer being resistant to hydrolysis; and
 - c) a passive resin that is soluble in the monomer.
2. The water-based, UV-curable ink as claimed in claim 1, wherein the monomer is hexane diol diacrylate.
3. The water-based, UV-curable ink as claimed in claims 1 or 2, wherein the passive resin is selected from the following list: solid epoxies, ketone resins, acrylate and methacrylate copolymers, vinyl resins, solid polyesters, phenoxy resins and cellulose; the passive resin preferably being an acrylate or methacrylate copolymer.
4. The water-based, UV-curable ink as claimed in claims 1, 2 or 3, wherein at least 25 parts by weight of passive resin are dissolved in the monomer.

5. The water-based, UV-curable ink as claimed in claims 1, 2, 3 or 4, wherein the ink comprises at least 10%, preferably at least 18%, more preferably at least 25%, of water, based on the total weight of the ink.

6. The water-based, UV-curable ink as claimed in any one of the preceding claims, wherein the passive resin has a Tg between 30 and 130°C.

7. The water-based, UV-curable ink as claimed in any one of the preceding claims, wherein the passive resin is present in the ink in an amount from 1-25%, preferably from 5-15%, by total weight.

8. A method for preparing a water-based, UV-curable ink that is capable of adhering to plastic substrates, the method comprising the steps of:

a) selecting a monomer that is capable of softening the plastic substrate in part or in full and is resistant to hydrolysis;

b) selecting a passive resin that is soluble in the monomer;

c) dissolving the passive resin in the monomer;

d) blending the passive resin and the monomer with a water-dispersible or water-soluble urethane acrylate oligomer, and

e) adding water to the blend.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 2126

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 95 28436 A (UNIV LEHIGH) 26 October 1995 * page 5, paragraph 1 * * page 8, paragraph 2 * * page 10, paragraph 3 * * page 12, paragraph 4 - page 13, line 2 * * page 20, paragraph 4 *	1-3,5,7	C09D11/10 C08F290/14
A	GB 2 270 917 A (SERICOL LTD) 30 March 1994 * the whole document *	1,2,5	
A	EP 0 026 313 A (BAYER AG) 8 April 1981 * claim 1 * * claim 3 * * claim 5 * * page 15, line 9 - line 10 *	1,2,5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09D C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 July 1997	Examiner Miller, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

EPO FORM 1503 01/92 (P04/C01)